

Experimental

4,4'-Diketodicyclohexyl (III).—Crude 4,4'-dihydroxydicyclohexyl (II), prepared from *p,p'*-diphenol (I) by high pressure hydrogenation over Raney nickel catalyst by the method of Adkins,³ was converted to (III) as follows. A mixture of 50 g. of (II), 50 ml. of diphenyl ether, and 13 g. of copper chromite catalyst was heated for three hours at 260–270°. During this time 70% of the theoretical quantity of hydrogen necessary for complete conversion to the diketone (III) was evolved. The reaction mixture was cooled and dissolved in chloroform. The solution was filtered to remove catalyst, and the filtrate was distilled. The fraction boiling from 144–170° (1 mm.) (which solidified on cooling) contained the product. Several crystallizations from mixtures of acetone and *n*-hexane gave a 16.5% yield of diketone (III); m. p. 116.5–118°. The purest material melted from 118–119°.

*Anal.*⁵ Calcd. for C₁₂H₁₈O₂: C, 74.18; H, 9.33. Found: C, 74.62; H, 9.53.

The diketone formed a dioxime; m. p. ca. 290° (copper block). The dioxime was practically insoluble in all ordinary organic solvents.

Anal. Calcd. for C₁₂H₂₀O₂N₂: C, 64.26; H, 8.98. Found: C, 64.82; H, 9.60.

bis-[3,3,5,5-Tetra-(β-cyanoethyl)-4-ketocyclohexyl] (IV).—To a solution of 18.4 g. of 4,4'-diketodicyclohexyl (III) in 80 ml. of dioxane containing 1.3 ml. of Triton B (38% aqueous solution of trimethylbenzylammonium hydroxide) there was added dropwise 41.5 g. of acrylonitrile (3% excess). The reaction mixture was vigorously stirred and maintained at room temperature by use of a water-bath during the addition. Yellow crystals were deposited as the reaction proceeded. After stirring overnight, the mixture was diluted with water and filtered, and the precipitated product was washed with acetone. Two or three crystallizations from formamide-nitromethane mixtures (ca. 80–20) gave 39 g. (66%) of white crystalline "octanitride" (IV); m. p. 280–287°.

Anal. Calcd. for C₃₆H₄₂O₂N₈: C, 69.86; H, 6.83; N, 18.11. Found: C, 69.86; H, 7.16; N, 18.05.

bis-[3,3,5,5-Tetra-(β-carboxyethyl)-4-ketocyclohexyl] (V) (Dicyclohexanoneoctopropionic Acid).—A suspension of 6.83 g. of the "octanitride" (IV) in 35 ml. of 85% aqueous phosphoric acid was heated for forty-eight hours on the steam-bath. Suspended matter dissolved as the hydrolysis proceeded, after which the clear solution gradually changed to a semi-solid mass. When hydrolysis was substantially complete, the reaction mixture was diluted with water, cooled and filtered. The precipitate was dissolved in alkali and the solution filtered. The filtrate on acidification gave fine white needles of the desired acid which, after recrystallization from water, weighed 5.82 g. (66% yield). Further purification consisting of (1) treating the acid with activated charcoal, (2) boiling in dilute hydrochloric acid solution (to hydrolyze any remaining nitrile groups) and (3) crystallizing from water followed by drying at 110° under reduced pressure was found necessary to secure a pure product; m. p. 274–277°, neutral equivalent 96.6, calcd. 96.3. On standing for several months in a desiccator, the melting point rose to 286–288°, probably due to a change in crystalline form.

Anal. Calcd. for C₃₆H₅₀O₁₈: C, 56.08; H, 6.54. Found: C, 56.05; H, 6.47.

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(3) H. Adkins, "Reactions of Hydrogen," University of Wisconsin Press, Madison, 1937, p. 58.

(4) All melting points are corrected.

(5) Analyses by Mr. Carl Parks of this Laboratory.

Preparation of Triethylacetonitrile and Triethylacetic Acid

BY CONRAD SCHUERCH, JR.,^{1,2} AND ERNEST H. HUNTRESS

Synthetic methods for the preparation of tertiary aliphatic acids or their simple relatives have not been correlated in the prior literature. They include, however, alkylation of aliphatic nitriles with alkyl bromides or chlorides in presence of sodamide,³ and the carbonation of RMgX compounds.⁴

For tertiary acids above dimethylethylacetic, carbonation of the appropriate RMgX compounds is not generally utilizable since the Grignard reagents prepared from higher halides usually react abnormally, yielding mixtures of alkanes and alkenes. Furthermore, the required carbinols are not commercially available and simple distillation is somewhat inadequate for removal of residual traces of the carbinols from their chlorides.

Our experience (Table I) in attempting to prepare tertiary acids by carbonation of tertiary-alkyl magnesium chlorides with either gaseous or solid carbon dioxide indicates that the yields of acids become progressively more unsatisfactory. The reactions were run on Grignards derived from 200–300 g. of alkyl chloride using the usual precautions^{4d}; yields are not necessarily optimal.

TABLE I

Acid	This work		Published work		Ref.
	Carbonylation with CO ₂ as	Yield, %	Carbonylation with CO ₂ as	Yield, %	
A. Trimethylacetic	Gas	67	Gas	61–70	4d
B. Dimethylethylacetic	Gas	40	Gas	60	4c
				Lower than (A)	4e
C. Methyl-diethylacetic	Solid	17	Not reported	42	4a
D. Triethylacetic	Solid	7	Not reported	Not reported	4a
E. 1-Methylcyclohexanecarboxylic	Solid	15	Gas	<25	4b

A better preparative process for triethylacetic acid was found in Ziegler's method³ for the alkylation of acetonitrile followed by subsequent purification and hydrolysis of the resultant triethylace-

(1) This paper is constructed from part of a dissertation submitted in June, 1947, by Conrad Schuerch, Jr., to the Faculty of the Massachusetts Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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(3) (a) Ziegler (to Schering-Kahlbaum, A. G.) U. S. Patent 1,958,653, May 15, 1933; C. A., **28**, 4435 (1934); British Patent 393,955, 394,087; C. A., **27**, 5755 (1933); German Patent 581,728, 583,561; C. A., **28**, 1057 (1934); French Patent 728,241; *Chem. Zentr.*, **104**, I, 1197–1198 (1933); C. A., **26**, 5573 (1932); (b) Ziegler and Ohlinger, *Ann.*, **495**, 84–112 (1932).

(4) (a) Whitmore and Badertscher, *THIS JOURNAL*, **55**, 1559–1567 (1933); (b) Gutt, *Ber.*, **40**, 2069 (1907); (c) Corson, Thomas and Waugh, *THIS JOURNAL*, **51**, 1950–1951 (1929); (d) Gilman, Kirby, "Organic Syntheses," Coll. Vol. I (2nd ed.), 361–364 (1941); (1st ed.) 353–356 (1932); Gilman and Parker, *ibid.*, **5**, 75–77 (1925); (e) Degnan and Shoemaker, *THIS JOURNAL*, **68**, 104 (1946).

tonitrile. Even when the alkylation was not carried out under pressure but merely at the boiling point of ethyl bromide where the principal reaction is dialkylation leading to diethylacetoneitrile, the yield of triethylacetoneitrile was sufficiently high to serve as a convenient preparative method.

In the course of our study of this procedure we also examined the behavior of acetoneitrile (1 mole) with ethyl bromide (excess) and sodamide (2-2.5 moles); acetoneitrile with diethyl sulfate in benzene (no alkylation); alkylation of a mixture of acetoneitrile with diethylacetoneitrile; and the behavior of *n*-butyronitrile with ethyl bromide (excess) in presence of sodamide (2 moles). The best conditions for the preparation of triethylacetoneitrile at ordinary pressure are concisely summarized below.

Triethylacetoneitrile.—To a mixture of acetoneitrile (61 g., 1.5 moles), ethyl bromide (408 g., 3.75 moles) and dry ether (100 ml.) in a creased 3-liter flask with high-speed stirrer was added a slurry of sodamide (117 g., 3 moles) in dry ether. This addition was effected under slight pressure of nitrogen during a one and one-half-hour period. Although no significant reaction occurred after this period, the mixture was stirred overnight and then cautiously treated with 50 ml. of alcohol, finally with water. After washing the ether solution with dilute sulfuric acid and finally with water, it was dried over magnesium sulfate and fractionally distilled at atmospheric pressure through a one-foot packed column. The products of mono, di and trialkylation were obtained as follows:

<i>n</i> -Butyronitrile	24.1 g.	0.348 mole	n_{D}^{21} 1.3838
Diethylacetoneitrile	35.2 g.	0.362 mole	n_{D}^{20} 1.4021
Triethylacetoneitrile	28.8 g.	0.23 mole	n_{D}^{20} 1.4219

Fractionation of the intermediate material and residue gave more of all three products.

Triethylacetic Acid.—Triethylacetoneitrile (60.3 g.) mixed with 75% sulfuric acid (106 g.) was raised to a temperature of 150° with constant stirring over a period of one-half hour. The temperature was then maintained at 145-150° for twenty-two more minutes after which the contents of the flask were cooled to 50°. Solid sodium nitrite (47 g.) was added from an attached flask during a period of about one hour at 50-60°. After cooling, diluting with water, and extracting with ether, the latter contained both the desired acid and its amide. The former was separated from the latter by extraction of the ether solution with aqueous 6% potassium hydroxide; yield of triethylacetic acid 56.6 g., 81.5%, purified with little loss by distillation under reduced pressure, b. p. 104-105° at 5 mm., f. p. 35.1°; yield of triethylacetamide 11.3 g., 17.6%.

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The Reaction of Certain β -Aminomercaptans with Iodine in Ethanol

BY H. R. SNYDER AND ERNEST L. ELIEL

In a recent report¹ on the synthesis of substituted mercaptans the derivatives obtained by reaction of certain β -aminomercaptans with iodine in alcohol were regarded as sulfenyl iodides. Shortly after the appearance of the report Pro-

fessor Norman Kharasch² kindly called to our attention the fact that the properties of the derivatives were not those to be expected of simple sulfenyl iodides and suggested that the substances were the dihydriodides of the disulfides formed by oxidation of the aminomercaptans.

A quantitative study of the reaction of alcoholic iodine with the mercaptan¹ [$C_6H_{12}NCH_2C(CH_3)_2SH$] obtained from β -pipecoline and isobutylene sulfide now has been made. The iodine consumption averaged 95% of that required for conversion of the mercaptan to the disulfide salt, or only 47.5% of the amount required for conversion to the sulfenyl iodide. The reaction also was carried out on a scale large enough to permit isolation of the product, conversion to the free disulfide by the action of sodium bicarbonate, distillation of the disulfide, and reconversion of the disulfide to the salt by treatment with hydriodic acid; the original salt was regenerated. The derivative previously obtained by the action of iodine on the aminomercaptan [(C_4H_9)₂NCH₂C(CH₃)₂SH] from di-*n*-butylamine and isobutylene sulfide was subjected to the same cycle (except that the free disulfide was not distilled). In this instance also the regenerated substance was identical with the original sample.

It thus appears certain that all the derivatives referred to as sulfenyl iodides in the previous report¹ are dihydriodides of diaminodisulfides having the general formula $[R_2NCH_2C(CH_3)_2S]_2 \cdot 2HI$. The previously recorded analyses of the substances are in good agreement with the theoretical values calculated on the basis of this structure.

Experimental³

Reaction of α, α -Dimethyl- β -(β -pipecolino)-ethyl Mercaptan with Iodine in Ethanol.—Samples of about 0.5 g. of the aminomercaptan¹ were dissolved in absolute ethanol and titrated with a standardized solution of iodine (0.1 *N*) in the same solvent. In four titrations the iodine consumption was 0.949, 0.950, 0.950 and 0.954 gram atoms per mole of mercaptan. The end-point was determined by the appearance of the iodine color. The preparative reaction was carried out essentially as described previously;^{*} the product (85% yield) melted at 210.5-211.5 (dec.).

Anal. Calcd. for $C_{20}H_{42}N_2S_2I_2$: C, 38.22; H, 6.73. Found: C, 38.02; H, 7.00.

The free disulfide was obtained by the addition of 50 ml. of saturated aqueous sodium bicarbonate solution to a solution of 7 g. of the above salt in 200 ml. of hot water, extraction of the cooled solution with ether, drying of the ether solution with sodium sulfate, removal of the ether, and distillation. The liquid (yield 2.7 g., 64%) boiled at 155-156° (3 mm.); n_{D}^{20} 1.5146; mol. wt. (ebullioscopic in benzene), 328 (calcd., 372.7).

The dihydriodide was regenerated by the addition of 0.6 ml. of hydriodic acid (sp. gr. 1.5) to 0.55 g. of the disulfide in 10 ml. of absolute ethanol. The salt crystallized immediately as a solid melting at 211-212.5° (dec.); recrystallization from ethanol raised the melting point to 212-213° (dec.). A mixture of the recrystallized salt with that prepared from the aminomercaptan and iodine

(2) Professor Norman Kharasch, the University of Southern California, Los Angeles; private communication, January 26, 1948.

(3) All melting points are corrected.

(1) Snyder, Stewart and Ziegler, *THIS JOURNAL*, **69**, 2672 (1947).